AD-A149 319 IMPROVED LITHIUM-INTERCALATION CATHODE MATERIAL(U) ECO 1/1
ENERGY CONVERSION NEWTON MA 01 NOV 84 N00014-84-C-0593

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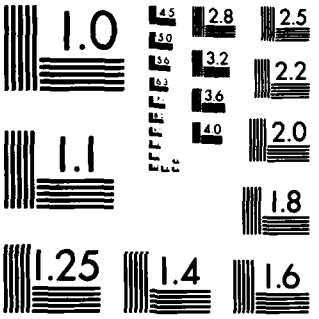

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November 1, 1984

Scientific Officer
Attn: Code 253, David S. Siegel
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217

Re: Contract No. N00014-84-C-593

Dear Dr. Siegel:

The following is submitted as an Interim Progress Report on an improved lithium-intercalation cathode material covering the period of August 1, 1984 to October 31, 1984.

I PROGRAM OBJECTIVE

The objective of the program is to determine the lithiation capacity and reversibility of four classes of functionalized tetraazaannulenes (TAAs).

II PROGRAM REPORT

1. Materials

The TAAs prepared included the cobalt forms of dibenzo TAA, di-(o-xylyl)-TAA, dibenzo-3,5,10,12-tetramethyl TAA and dibenzo-4,11-ditoluyl TAA, as well as dibenzo-4,11-azophenyl TAA. These materials were prepared by the general reaction of an aldehyde with a refluxing solution (ethanol:methanol) of an amine and cobalt acetate. The materials obtained were characterized by IR.

Cathodes were prepared by physically mixing the TAA (25 to 75 w/o) with carbon [Vulcan XC-72, Shawinigan Acetylene Black (SAB), or graphite] and PTFE (10 w/o) in a minimum volume of isopropanol or cyclohexane, and applying the paste to the nickel screen (4.5 cm^2) to a uniform thickness (approx. 0.06 cm). After drying at 90°C overnight, the electrode was used in an electrode stack with an anode (4.5 cm^2 Li foil on nickel screen) and reference electrode (0.5 cm^2 Li foil on nickel wire). Microporous fiber glass separators were used. The electrolyte used was either 1.5 M $LiAsF_6$/2-MeTHF or 1.0 M $LiAsF_6$/2,4-dimethyl-1,3-dioxolane which were purified by reflux over 5 a/o Li(Hg) under argon.

The cells were assembled under a dry argon atmosphere (glove box), sealed, and discharged (or charged) at constant current (0.2 mA/cm^2). Load voltage was recorded using an ECD VT30/0 data logger with ten channel multiplexer.

2. Reactions with n-Butyl Lithium

Samples of each of the five TAAs were reacted with n-butyl lithium in n-hexane. This reaction was characterized by a darkening in solution color. Based on an analysis of gas produced and elemental analysis of the residual solids, less than one equivalent of lithium intercalated. When the analogous reactions were tried in THF, the metallated TAAs acted as catalysts for the solvolytic reaction between THF and n-butyl lithium. When the unmetallated TAAs were used, the dilithio intercalate appeared to be formed (based on elemental analysis).

3. Electrochemical Lithiation

Cathodes containing 25 w/o of the TAAs were discharged to a 1.0 V vs reference cut-off; the level of lithium intercalation was determined based on the discharge capacity observed. Provided in Table 1 is a list of the equivalents of lithium intercalated as a function of TAA. Two of the five TAAs are apparently capable of significant levels of lithium intercalation. At these levels, the theoretical electron equivalent weight of such TAAs is improved (30%) compared to TiS_2. Further work is underway to evaluate whether the electrode structure used is limiting the TAA intercalation capacity.

III FUTURE WORK

During the next half of the program, ECO will evaluate cycle life, lithium diffusion rate, and self-discharge rates of the five TAAs.

Sincerely,

Fraser Walsh

FW:nck

Table 1

Equivalents of Lithium Intercalated Electrochemically

TAA	Li Equivalents
CoTAA	8
Co bisazophenyl TAA	10
Co bistoluyl TAA	2
Co dixylyl TAA	1
Co tetramethyl TAA	1

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